

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Consequences of the 'jacketed' effect on mesomorphic and orientational properties of 'side-on fixed' liquid crystalline polymers

N. Leroux^a; M. F. Achard^a; P. Keller^b; F. Hardouin^a

^a Centre de Recherche Paul Pascal, Université Bordeaux I, Pessac, France ^b Laboratoire Léon Brillouin, Gif sur Yvette, France

To cite this Article Leroux, N. , Achard, M. F. , Keller, P. and Hardouin, F.(1994) 'Consequences of the 'jacketed' effect on mesomorphic and orientational properties of 'side-on fixed' liquid crystalline polymers', *Liquid Crystals*, 16: 6, 1073 – 1079

To link to this Article: DOI: 10.1080/02678299408027876

URL: <http://dx.doi.org/10.1080/02678299408027876>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Consequences of the 'jacketed' effect on mesomorphic and orientational properties of 'side-on fixed' liquid crystalline polymers

by N. LEROUX, M. F. ACHARD, P. KELLER† and F. HARDOUIN*

Centre de Recherche Paul Pascal, Université Bordeaux I,
Avenue A. Schweitzer, F-33600 Pessac, France

† Laboratoire Léon Brillouin, CEA-CNRS/CE Saclay, F-91191 Gif sur Yvette, France

(Received 6 August 1993; accepted 6 December 1993)

The mesomorphic properties have been studied as a function of the degree of polymerization for certain 'side-on fixed' polyacrylates. A peculiar evolution of the clearing temperature, T_{IN} , as well as of the glass transition temperatures, T_g , revealed that beyond a certain backbone length, T_{IN} and T_g decrease as the main chain length increases. The nematic 'jacketed' structure of these polymers induces a more or less high anisotropy of the polymer backbone conformation in the nematic phase and this can counterbalance the usual effect of an increase in the degree of polymerization on the thermodynamical properties of these systems. This evolution allows us to explain the unusual diamagnetic anisotropy anomaly observed as a function of temperature for this type of polymer.

1. Introduction

'Side-on fixed' liquid crystalline polymers form a peculiar class of side-chain mesomorphic polymers in which the mesogenic moieties are laterally fixed to the polymer backbone in the direction perpendicular to their molecular long axes via a flexible spacer (see figure 1). They generally exhibit only the nematic phase [1–6].

Previous small angle neutron scattering studies on these polymers have shown their strong tendency to adopt a highly prolate conformation in the nematic phase and clearly revealed the so-called nematic 'jacketed' effect resulting in a large main chain extension in the direction of the external magnetic field, the mesogenic groups forming a jacket around the backbone [7–11].

This polymer anisotropy is clearly influenced by the nature [9] and the length of the backbone [8], by the spacer length [9] and by the mesogen density along the main chain [8, 10]. Specifically, the influence of the 'jacketed' structure decreases as the backbone length or the spacer length increases and as the fixation rate of the mesogenic groups on the backbone decreases.

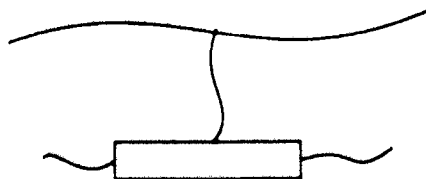


Figure 1. Schematic representation of a 'side-on fixed' polymer.

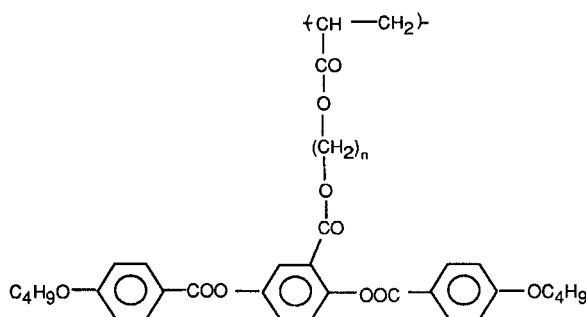
* Author for correspondence.

Besides this, diamagnetic anisotropy measurements on 'side-on fixed' polysiloxanes have revealed an anomaly in the thermal evolution of the diamagnetic anisotropy in the nematic state [4, 6]. The existence of this anomaly is strongly connected to structural parameters: an increase in the spacer length [4] or in the length of the aliphatic tails [6], or a diminution in the fixation rate of the mesogenic moieties on the backbone [6] leads to the disappearance of this anomaly.

In this paper, our aim is to investigate the possible influence of the nematic 'jacketed' structure both on the mesomorphic and the orientational properties of 'side-on fixed' polymers. Two parameters which strongly modify the strength of the jacketed effect have been varied, namely the length of the backbone and the length of the spacer.

2. Mesomorphic properties

The polymers investigated have the following general formula:



These polyacrylates are labelled $PA_{n,4,4}$ where n is the spacer length ($n=4$ or 6).

The average molecular weights (\bar{M}_w) and the polydispersity index (I) were determined by analytical Gel Permeation Chromatography (GPC) using three 7.8×300 mm Ultrastaygel columns of 10^4 , 10^3 and 500 \AA (from Waters Associates) with toluene as eluant. The calibration was done with standard polystyrenes. As the molecular weight distributions of the crude materials were broad (see table 1), successive fractionations were performed using a semi-preparative GPC (19×300 mm Ultrastaygel column of 10^4 \AA) using toluene as eluant.

The average molecular weights (\bar{M}_w) and the polydispersity indices (I) of the fractions were determined by analytical GPC with respect to polystyrene calibration. As seen in table 2, the set of fractionated samples allowed us to scan a large range of degrees of polymerization. The polydispersity is considerably reduced by comparison with the crude materials. However, to achieve a further significant decrease in the polydispersity index would involve numerous additional fractionations and very large amounts of available starting materials. Note that the $PA_{6,4,4}$ has undergone fewer successive fractionations.

The transition temperatures measured by optical microscopy for each fraction (see table 2) correspond to the first appearance of the nematic phase with decreasing temperature (1°C min^{-1}) from the isotropic liquid. In agreement with the I values, we still observe a small biphasic region at the isotropic-nematic transition. The glass transition temperatures T_g determined by DSC (Perkin-Elmer DSC7, heating rate $10^\circ\text{C min}^{-1}$) are also reported in table 2.

Two striking features are immediately obvious from the data in table 2: they concern the evolution of the transition temperature T_{IN} and of the glass transition temperature T_g as a function of the degree of polymerization. As usually observed for

Table 1. Average molecular weight (\bar{M}_w), polydispersity index (I) and clearing temperature (T_{IN}) for the two polyacrylates PA_{4,4,4} and PA_{6,4,4}.

Crude polymer	\bar{M}_w	I	$T_{IN}/^\circ\text{C}$
PA _{4,4,4}	40000	2.7	113
PA _{6,4,4}	40000	3.7	106

Table 2. Average molecular weight (\bar{M}_w), polydispersity index (I), average degree of polymerization (\overline{DP}_w) clearing temperature (T_{IN}) and glass transition temperature (T_g) for the fractions of the two polyacrylates PA_{4,4,4} and PA_{6,4,4}.

PA _{4,4,4}					PA _{6,4,4}				
\bar{M}_w	\overline{DP}_w	I	$T_{IN}/^\circ\text{C}$	$T_g/^\circ\text{C}$	\bar{M}_w	\overline{DP}_w	I	$T_{IN}/^\circ\text{C}$	$T_g/^\circ\text{C}$
83000	129	1.2	108.8	37	137000	206	1.5	102.5	36
66200	103	1.2	112.9	40	107000	160	1.5	105.3	37
56100	87	1.3	113.5	44	67000	101	1.3	106.7	38
45100	70	1.2	113.2	48	37000	56	1.4	106	38
32800	51	1.5	113.1	49	22000	33	1.7	103.5	36
26700	42	1.5	112.1	49	8300	12	1.5	92	31
24100	38	1.6	111.2	49					
16300	25	1.6	105.3	47					
11200	17	1.5	101.3	46					
7800	12	1.5	98.3	45					

side-chain liquid crystalline polymers, T_{IN} first increases with the degree of polymerization, reaching a plateau. But as the degree of polymerization further increases, we observe an unusual diminution of the transition temperature (see figure 2). A similar behaviour has been suggested for some new polynorbornenes [12].

As shown in figure 3 a comparable evolution is evident for the glass transition temperature versus the degree of polymerization. Such a decrease of T_g has been already reported for side-on fixed polysiloxanes [8].

These unusual behaviours could be closely related to the 'jacketed' effect which was recognized to be less efficient for long polymer backbones (probably due to elbows or hairpins) [8]. Indeed, the isotropic to nematic phase transition temperature plateau is observed for polymers with medium \overline{DP}_w which exhibit a significant anisotropy of the global main chain conformation, with an extension in the direction of the nematic director. For larger degrees of polymerization, the chain anisotropy weakens and hence the clearing temperatures decrease.

These unusual evolutions of T_{IN} and T_g are observed for both spacers ($n=4$ and 6): beyond a certain degree of polymerization, the clearing temperature and the glass transition temperature decrease as \overline{DP}_w increases. Nevertheless, a quantitative difference seems noticeable between the two spacers: T_{IN} , as well as T_g , decreases more steeply for the shorter spacer ($n=4$). The spacer length influence on the behaviour of these temperatures can be connected to the earlier result on 'side-on fixed' polyacrylates [9]: the shorter the spacer, the stronger is the nematic 'jacketed' effect. The particular structure of 'side-on fixed' polymers creates strong interactions between the main chain and the mesogenic cores, so that the mesomorphic properties are highly

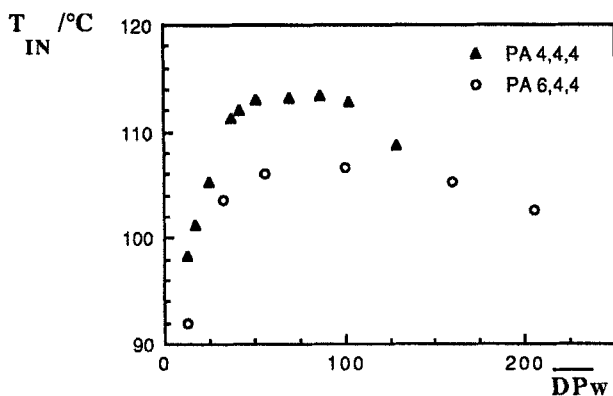


Figure 2. Evolution of the isotropic–nematic transition temperature as a function of the average degree of polymerization for the two polyacrylates PA_{4,4,4} and PA_{6,4,4}.

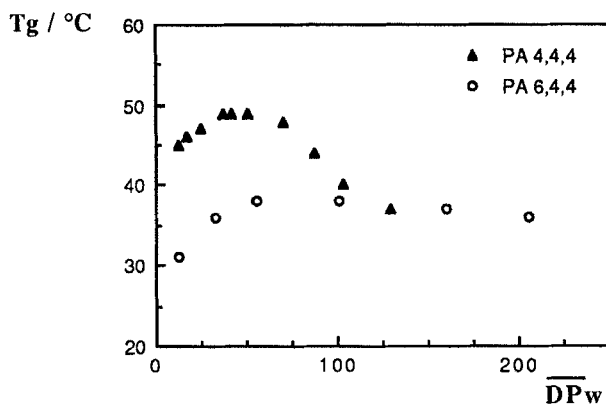


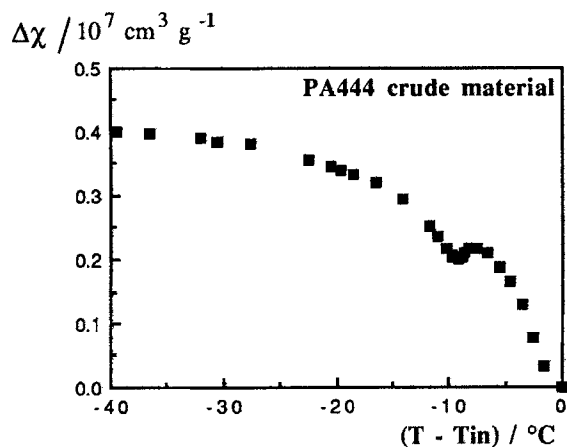
Figure 3. Evolution of the glass transition temperature as a function of the average degree of polymerization for the two polyacrylates PA_{4,4,4} and PA_{6,4,4}.

influenced by the global conformation of the system. Therefore the nematic ‘jacketed’ effect plays a decisive role in controlling the nematic phase organization.

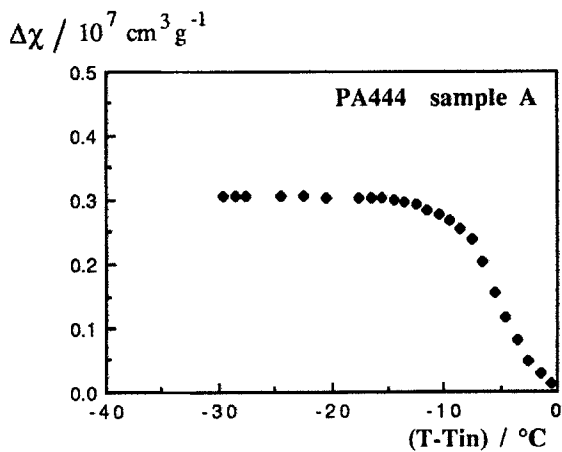
Because of this unusual decrease in the clearing temperatures of ‘side-on fixed’ polyacrylates, a new explanation for the diamagnetic anisotropy anomaly can be now considered: on decreasing the temperature from the isotropic state, the first isotropic–nematic transformation will be due to the polymer molecules with medium degrees of polymerization. The resulting monodomain at equilibrium can be disturbed (probably due to entanglement) by the alignment process of the longest chains at lower temperatures. Therefore we could explain the anomaly by a combination of some molecular weight heterogeneity and the ‘jacketed’ effect, so creating a non-regular orientation of the system in the nematic phase. A good way to prove this assumption is to make diamagnetic anisotropy measurements on ‘side-on fixed’ polymer fractions with different molecular weights, especially with a short spacer, leading to a strong nematic ‘jacketed’ effect.

3. Diamagnetic anisotropy measurements

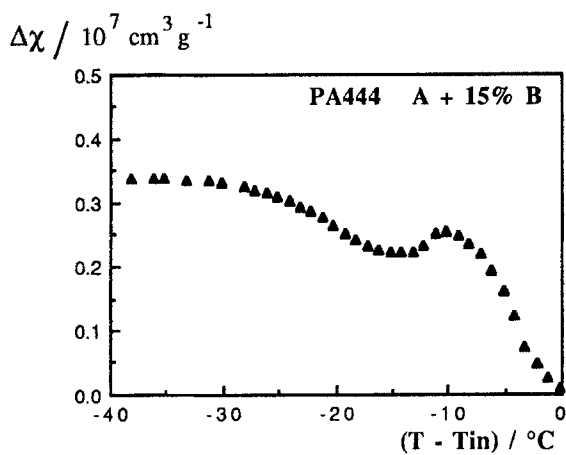
The diamagnetic anisotropy $\Delta\chi$ was evaluated for the nematic phase from measurements of the diamagnetic susceptibility in the direction parallel to the magnetic



(a)



(b)



(c)

Figure 4. Thermal evolution of the diamagnetic anisotropy $\Delta\chi$ (a) for the crude polyacrylate $PA_{4,4,4}$, (b) for fraction A ($\overline{DP}_w=15$, $I=1.7$) of the polyacrylate $PA_{4,4,4}$ and (c) for fraction A containing 15 wt% of fraction B ($\overline{DP}_w=60$, $I=1.3$).

field, $\chi_{\parallel H}$, using a Faraday Balance [13]

$$\Delta\chi = 3/2(\chi_{\parallel H} - \bar{\chi}),$$

where $\bar{\chi}$ is the average susceptibility measured in the isotropic state.

The magnitude of the magnetic field was 1.5 Tesla. In a uniaxial nematic phase, this expression represents the macroscopic order parameter which is directly connected to a single orientational order parameter which has been introduced in the Maier and Saupe theory [14] under certain conditions, namely that the molecules must have a cylindrical symmetry and that no change of the molecular shape occurs with temperature.

The magnetic measurements, described here, were carried out as a function of temperature for the 'side-on fixed' polyacrylate PA_{4,4,4}. The information they give is only qualitative since they have been realized without any kinetic treatment. In particular, we obtain values of $\Delta\chi$ at low temperature which are probably not the saturated values.

Originally, the crude polydisperse PA_{4,4,4} exhibits an anomaly (see figure 4(a)). Then we studied a fraction labelled *A*, with a small average degree of polymerization ($\overline{DP}_w = 15$, $I = 1.7$) and whose highest molecular weight is still low ($M_{\max} = 20\,000$), so that it corresponds to the region having an usual T_{IN} evolution. The result is reported in figure 4(b). Obviously there is no anomaly in the thermal evolution of the diamagnetic anisotropy; this sample *A* which does not have any high molecular mass content, exhibits the usual evolution of $\Delta\chi$. Thus it appears that no anomaly occurs for short polymer chains.

To study the influence of molecular weight on the thermal evolution of $\Delta\chi$, we added to the sample *A* 15 wt per cent from a fraction of the same polyacrylate, labelled *B*, which has on average a higher degree of polymerization ($\overline{DP}_w = 60$, $I = 1.3$) and whose highest molecular weight is large and corresponds to the \overline{DP}_w region exhibiting an unusual decrease in T_{IN} . An anomaly in $\Delta\chi$ is again detected (figure 4(c)). This observation is quite new: from a normal behaviour observed for the thermal evolution of the diamagnetic anisotropy for a low molar mass 'side-on fixed' polymer, an anomaly in $\Delta\chi$ is created by the presence, even in small proportions, of the same polymer corresponding to a higher molecular mass fraction.

Thus we have evidence for the influence of the dispersity of the molecular weight, via the 'jacketed' effect, on the anomaly of the thermal evolution of the diamagnetic anisotropy. The presence in small proportions of long polymer backbones can explain the unusual behaviour of $\Delta\chi$ as long as the 'jacketed' effect is relevant. This was notably the case for the 'side-on fixed' polysiloxanes previously studied [4, 6, 8]. For example, the polysiloxane which has the same mesogenic group as that used here, with a spacer length equal to 4, and whose average molecular weight was about 42 000 [6], included a small amount of materials with molecular weights up to 86 000; this system is strongly 'jacketed' in the nematic phase [8] and exhibits an anomaly in the thermal evolution of $\Delta\chi$. Therefore this 'artefact' of the orientational order is a natural consequence of the 'jacketed' effect, which depends on the polymer size.

4. Conclusions

'Side-on fixed' liquid crystalline polymers offer a class of nematic polymers which exhibit a more or less pronounced 'jacketed' effect depending on molecular parameters. Increase in the degree of polymerization, which generally tends to increase the clearing temperature and the glass transition temperature, is balanced in such 'side-on

fixed' polymers by the opposing influence of the decrease in the anisotropy of the polymer by reduction of the 'jacketed' effect.

Consequently, this unusual main chain length dependence of the thermal properties allows us to explain the diamagnetic anisotropy anomaly previously reported in the high temperature range of the nematic phase.

Finally, it is worth noting that for the same mass distribution (in polysiloxanes synthesized from the same preformed backbone) the amplitude of this anomaly decreases as the 'jacketed' effect decreases, for example, by increasing the length of the spacer or the aliphatic tails or by reducing the proportion of the mesogenic units along the main chain [6].

References

- [1] HESSEL, F., and FINKELMANN, H., 1985, *Polym. Bull.*, **14**, 375.
- [2] QI-FENG ZHOU, HUI-MIN, and XI-DE FENG, 1987, *Macromolecules*, **20**, 233.
- [3] HESSEL, F., and FINKELMANN, H., 1988, *Makromolek. Chem.*, **189**, 2275.
- [4] KELLER, P., HARDOUIN, F., MAUZAC, M., and ACHARD, M. F., 1988, *Molec. Crystals liq. Crystals* **155**, 171.
- [5] GRAY, G. W., HILL, J. S., and LACEY, D., 1990, *Molec. Crystals liq. Crystals*, **7**, 47.
- [6] HARDOUIN, F., MERY, S., ACHARD, M. F., MAUZAC, M., DAVIDSON, P., and KELLER, P., 1990, *Liq. Crystals*, **8**, 565.
- [7] HARDOUIN, F., MERY, S., ACHARD, M. F., NOIREZ, L., and KELLER, P., 1991, *J. Phys. II, France*, **1**, 511; 1991, *Ibid.*, **1**, 871 (erratum).
- [8] HARDOUIN, F., LEROUX, N., MERY, S., and NOIREZ, L., 1992, *J. Phys. II, France*, **2**, 271.
- [9] LEROUX, N., KELLER, P., ACHARD, M. F., NOIREZ, F., and HARDOUIN, F., 1993, *J. Phys. II, France*, **3**, 1289.
- [10] LEROUX, N., MAUZAC, M., NOIREZ, L., and HARDOUIN, F., 1994, *Liq. Crystals*, **16**, 421.
- [11] CHERODIAN, A. S., HUGHES, N. J., RICHARDSON, R. M., LEE, M. S. K., and GRAY, G. W., 1993, *Liq. Crystals*, **14**, 1667.
- [12] PUGH, C., and SCHROCK, R., 1992, *Macromolecules*, **25**, 6593.
- [13] REGAYA, B., and GASPAROUX, H., 1971, *C. r. hebd. Séanc. Acad. Sci., Paris*, **272B**, 724.
- [14] MAIER, W., and SAUPE, A., 1959, *Z. Naturf. (a)*, **14**, 882; 1960, *Ibid.*, **15**, 287.